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Investigating FAIMS Response to Trihalomethanes with Respect to Humidity

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1. Introduction

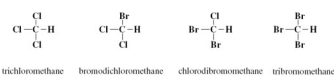
The disinfection of potable water has dramatically reduced the instances of Cholera and similar ailments within a population drawing upon that water source. There is however the possibility that Natural Organic Matter (NOM) can interact with the disinfection compounds to form Disinfection By-Products (DBP) [1]. One group of DBPs are Trihalomethanes (THMs) with several compounds of the group being suspected carcinogens. Within the UK the total concentration of all THMs within drinking water must not exceed 100µg/l.

At present water authorities take samples of the water supply and return them to a central laboratory for analysis. This provides an accurate test but one which can involve a long lead time in discovering a potential hazard to public health.

A Field Asymmetric Ion Mobility Spectrometer (FAIMS) sensor may be ideally placed to perform *in situ* continuous monitoring at particular sites. As part of a PhD co-sponsored by The Open University and Owlstone Nanotech Plc an investigation is ongoing to discover how sensitive a FAIMS device is with respect to THMs and humidity when sampling. Initial results and the method of data processing, which involves peak fitting to evolving spectra are presented.

2. Trihalomethanes and FAIMS

The formation of THMs is dependent upon the location of the water reserve. Open air reservoirs and bore holes will have different exposures to factors such as agricultural run-off and therefore the formation of a particular THM will vary from one location to the next. There are four THMs of particular interest since they are formed from the typically most abundant halides Chlorine and Bromine, their structures are presented below.



As mentioned within the introduction the total permitted abundance of THMs within UK drinking water is 100µg/l [1] (80µg/l in the US under new regulations [2]). Therefore it is a requirement that all THMs can be detected.

There have been previous studies of systems incorporating FAIMS with the detection of THMs within drinking water. Of particular note are the extremely sensitive readings from Ellis *et al* [3]. These studies however used a FAIMS system as a preliminary stage to a mass spectrometer. To provide a significant step to what is already accomplished through sampling and analysis within the lab it is required that the detection be completed *in situ*. This will reduce the time taken to take appropriate action given an excessively high level of THMs within the potable water supply.

A stand alone FAIMS system may provide the ideal solution. While the system would not be as sensitive as when used in conjunction with additional technologies such as gas chromatography and mass spectrometry it would be able to operate at ambient conditions of temperature and pressure. The system used within this investigation incorporated the Owlstone Nanotech FAIMS chip [4] which is a miniaturised solid state device. The sensing technology employed therefore has the integral properties of a small size, low power requirement and high reliability.



Landscape Reservoir

3. Experimentation

The limit of detection of the THMs and the FAIMS response with respect to concentration were quantities that were to be determined. It was therefore the case that an exponential dilution flask (EDF) experiment [5] was used for the investigation.

EDF experiments consist of a sample flask which is continuously flushed with a flow. Analyte is introduced into the flask, typically through an injection, and over time the concentration of the analyte will be continuously diluted by the incoming flow. The concentration of analyte within the EDF is expressed through the equation,

$$C = C_0 \exp\left(-\frac{ut}{V}\right)$$

C_0	Initial concentration	mg/l
C	Concentration at time t	mg/l
u	Flow rate through EDF	ml/min
t	Time since injection	min
V	Volume of EDF	ml

It is therefore possible to easily generate a large range of known concentrations.

An Owlstone Lonestar unit was used to sample the EDF allowing the response of a FAIMS system with respect to varying concentration of THMs to be observed.

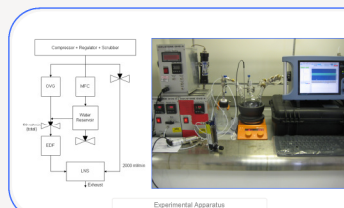
The sample line from the EDF to the Lonestar and the EDF itself was maintained at an elevated temperature throughout data collection

Two airflows were passed into the EDF. One was a clean and dry air line while the second was a clean and dry air line which also passed through a bubbling water bottle. Through the control of needle valves the humidity within the EDF was managed.

The Lonestar system required a carrier gas of clean dry air. While the system can operate by drawing on ambient air, the unit was provided with clean and dry air to remove the possibility of any degradation to the scrubber during the investigation. Ionisation was provided through a 555MBq ⁶³Ni source.

Through initial testing a suitable dispersion field was discovered which provided good separation of ion species at an acceptable sensitivity. Data was recorded with the dispersion field as a constant to minimise the variables. It was therefore possible to observe the formation and evolution of separate ion species across a large concentration range.

In between experiments the instrumentation was left to flush through to mitigate against any residual analyte from the previous data collection affecting later runs.

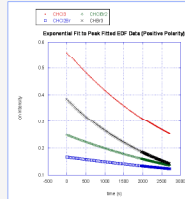
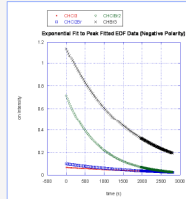


Experimental Apparatus



Owlstone Lonestar

6. Discussion and Further Work



An initial surprise was the strong positive polarity response to the introduction of the THMs. The strongest signal was found from the small and symmetrical Chloroform compound. After this however the system appears to be more sensitive with increasing amounts of bromine present

The limits of detection are too high to be of immediate use to the water industry. Modest pre-concentration, such as purge and trap, may provide the required LOD and provide the method of sampling needed to remove the THMs from the water for analysis [6].

Limit of detection (µg/l)	CHCl ₃	CH ₂ ClBr	CHCl ₂ Br	CHBr ₃
Positive polarity	750	1500	1100	1000
Negative polarity	5500	4270	3000	2200

This investigation was constructed to investigate not only the FAIMS response to THMs but also the effect humidity has on that response. Unfortunately the experimental set-up resulted in a very small range of humidities which proved stable. The EDF was therefore either very dry (< 6ppm water) or saturated.

- initially starts with low humidity and then later saturated levels. The high humidity appears to stabilise the ion species formed.
- displays the unique CV positions resulting from each THM. Future studies are being prepared which provide a constant flow of analyte via a permeation source and so water can be injected into the EDF providing the well characterised humidity variation.

4. Data Processing

The response from the FAIMS device is made up of many compensation voltage (CV) spectra. Each sweep of compensation voltage provides a snapshot of the ion species present at that particular time of scanning. These spectra contain Gaussian peaks due to the ion species present.

The response is gathered through a Faraday cup which provides a summed response of the Gaussian curves. The compensation voltage of the Gaussian peaks within a FAIMS device are known to be dependent upon the identity of the ion species present. It is therefore of special interest to obtain the most accurate determination of compensation voltage position as possible.

Since the response from each ion species is summed, any response which results in two or more Gaussian curves overlapping with one another will result in the true position and intensity of the peaks being a result of the mixing Gaussians. Deconvolution of the signal is required to obtain the true CV position and intensity of the mixed responses. Peak fitting can be used to discover the most likely initial Gaussian responses which have resulted in the amalgamated response provided by the FAIMS system.

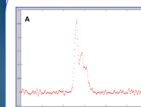
Within FAIMS studies the observation of a Gaussian peak is often attributed to a single ion species. When FAIMS has been used as a preliminary stage to mass spectrometry it is often observed that there are in fact several ion species responsible for a single Gaussian observed.

With this knowledge it is tempting to fit as many Gaussians as possible to the data in the hope of being able to uncover underlying features. The result of this process is often to create fits which no longer correspond to the features of the raw data.

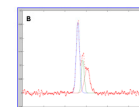
It is important to limit the number of peak fits to the easily identifiable number of peaks present from the raw data and from known or anticipated chemical reality [5]. This will mean mass spectrometry will always be required to identify the exact constituents of peaks. However, for many purposes fitting a low number of peaks allows us to identify trends within a data set. Also the improved CV positions and ion intensity values are still extremely relevant for investigations.

The spectra shown in section 5 are single CV sweeps. If the relevant values of CV position and ion intensity are recorded for each single sweep and plotted with respect to time we can observe how they evolve over time. Two important quantities can now be discerned from each EDF run, the CV position of peaks resulting from THMs and the limit of detection of the system.

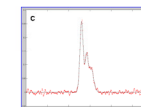
5. Peak Fitting



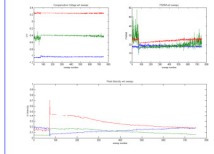
A) The raw data undergoes a stage where the baseline is corrected back to zero. This is required due to the effects of the electronics of the system.



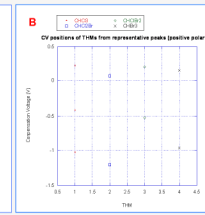
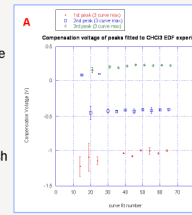
B) The data is then automatically preliminarily inspected by an algorithm which determines the maximum number of peaks within the sample. The algorithm is purposefully designed to compensate for mixed peaks and also returns the likely CV position, ion intensity and FWHM of each peak. This information is then passed on to a more advanced system utilising an unconstrained multivariable function using derivative-free method. This provides the final peak fit.



C) The fitted peaks are judged by whether the sum of the fits is close to, but does not exceed the output from the Faraday cup. This displays a good fit and it can be seen from the second tile that the fitted peaks are slightly different to the main peaks in the raw data.



Above is the result of plotting the ion intensity, CV position and FWHM of each fitted peak from each sweep with respect to sweep number (hence time). From this information the ion species present can be inferred and the limits of detection calculated.



[1] Xie, Y.P. Disinfection By-Products in Drinking Water. 2004.
[2] Environmental Protection Agency. National Primary Drinking Water Regulations: Disinfectants and Disinfection By-Products. In: Federal Register. December 16, 1998 (Volume 63, Number 241). Rules and regulations. 1998. p. 69300-69476.
[3] Ellis, B. *et al*. Detection of chlorinated and brominated disinfection by-products using electrospray ionization-high-field asymmetric waveform ion mobility spectrometry-mass spectrometry. Analytical Chemistry. 1999; 71(20): p. 4147-4152.
[4] Boyle, B. *et al*. A MEMS fabricated device for field asymmetric ion mobility spectrometry. Proceedings of the 5th Ph.D. Conference, New Orleans, LA, 2008.
[5] Linstedt, J.E. Injection Methods for the Analysis of Gases and Vapors. Analytical Chemistry. 1991; 63(2): p. 142-147.
[6] Dennis, N. Davis, C.B., Donald, B. Smith, Suzanne E. Bell, Gary A. Eisenman, Robert G. Ewing. Analysis of ion mobility spectra for mixed vapors using Gaussian deconvolution. Analytica Chimica Acta. 1994; 289(3): p. 263-272.
[7] Hsieh, C. and R. Kretzschmar. Strong anion-cation interaction in the detection of organic anions by electrospray ionization mass spectrometry. In: Electrospray Ionization. 1999. p. 3369-3371.
Images: Landscape Reservoir, www.yorkshirefishing.org.uk/blog; Owlstone Lonestar, www.owlstonenano.com

